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UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	L	liter
°F	degree Fahrenheit	min	minute
ft	foot	mL	milliliter
gal/ton	gallon per ton	mm Hg	millimeter of mercury
g	gram	N	normal (concentration)
g/L	gram per liter	pct	percent
hr	hour	wt-pct	weight-percent
in	inch		

CAUSTIC EXTRACTION OF ALUMINA AND SODA FROM DAWSONITE-BEARING OIL SHALE

By Gene Asai,[1] J. E. Mauser,[1] R. L. Lincoln,[2] and Jack L. Henry[3]

ABSTRACT

The Bureau of Mines investigated the caustic extraction of alumina and soda from retorted dawsonite-bearing oil shale, as part of a program to devise technology for treating alternative domestic sources of alumina for the production of aluminum metal. Colorado oil shale yielding 13 pct oil (35 gal/ton) and containing 12 wt-pct dawsonite (representing about 4 pct extractable alumina) was retorted to obtain oil-free (spent) shale. Spent shale was leached with dilute NaOH to determine the effect of particle size, retorting temperature, leaching variables, and storage conditions on extraction of alumina and soda and dissolution of impurities.

Maximum alumina and soda extractions were obtained by promptly leaching minus 28-mesh spent shale, obtained by retorting raw shale at about 500° C, with 0.5N NaOH. Under these conditions, dissolution of impurities such as Ca, Fe, Ti, and P was low. Leaching tests were made on spent shale stored for periods of up to 30 days at 0° to 42° C and at 0 to 100 pct relative humidity (RH). These tests indicated that significant reductions in alumina extraction would occur if spent shale were stored in ambient Colorado air under naturally fluctuating temperature and humidity.

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INTRODUCTION

Nearly all of the bauxite ore used in domestic aluminum production is imported because there are no extensive domestic bauxite deposits. Although the foreign supply is adequate for many years, it is desirable to devise technology for obtaining alumina (Al_2O_3) from alternate resources in case of emergencies and also to discourage unwarranted price increases. To address this problem, the Bureau of Mines has investigated processes for extracting alumina from clay (4)[4] and other domestic resources. The investigation described herein is among those in a Bureau program to obtain maximum recovery of mineral values from domestic resources.

One of the domestic resources for alumina is the oil shale deposits in the Piceance Creek Basin of Colorado. In addition to containing vast quantities of oil, some of these deposits contain the mineral nahcolite ($NaHCO_3$) and an alumina-bearing mineral, dawsonite [$NaAl(OH)_2CO_3$] (2, 5). It is estimated that a total resource of 29 billion tons of nahcolite (containing 10.7 billion tons of soda (Na_2O)) and 19 billion tons of dawsonite (containing 6.5 billion tons of alumina and 4.1 billion tons of soda) are present in the oil shales of Colorado's Piceance Creek Basin (1). This resource could supply domestic alumina needs for hundreds of years. (Domestic consumption of alumina in 1979 was about 14 million tons.)

There are some economic problems associated with extraction of alumina from dawsonite-bearing oil shale. The percentage of extractable alumina is low, and as shown in figure 1, the deposits are deeply buried. Most of the extractable alumina originates from decomposed dawsonite. With an average dawsonite content of 10 to 12 pct, the extractable alumina content is only about 4 to 5 pct. However, if the costs for mining and retorting shale are charged to shale oil, the economic feasibility for alumina and soda ash extraction would be improved.

There has been no commercial exploitation of dawsonitic shale for oil, nahcolite, and alumina. However, the technology for recovering nahcolite, alumina, and soda has been investigated on a samll scale. The U.S. Department of the Interior (2, 6), The Oil Shale Co. (TOSCO) (3), Multi-Minerals Corp., and Superior Oil (11) have published procedures for recovering values. Crushed shale is retorted to obtain oil-free (spent) shale that is leached with dilute base and filtered, and alumina trihydrate is precipitated from the solution. Sodium carbonate remaining in the solutions after precipitation of alumina trihydrate may be recovered by established crystallization procedures. For deposits with high nahcolite content, most of the more friable nahcolite is recovered by physical separation from the smaller size fractions in the crushed shale. However, much of the published information is qualitative and incomplete with respect to details for the development of a complete process.

There was a need for more quantitative information on the following:

1. The effect of shale particle size on alumina and soda extraction;

2. The effect of spent shale storage conditions, especially moisture, on alumina and soda extraction; and

3. The extent of dissolution of unwanted impurities in dilute NaOH.

With the availability of a 100-ton sample of dawsonite-bearing oil shale mined from the Bureau of Mines shaft at Horse Draw in the Piceance Creek Basin, the Bureau began a laboratory investigation to study the caustic extraction of alumina and soda as affected by retorting and leaching variables.

[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

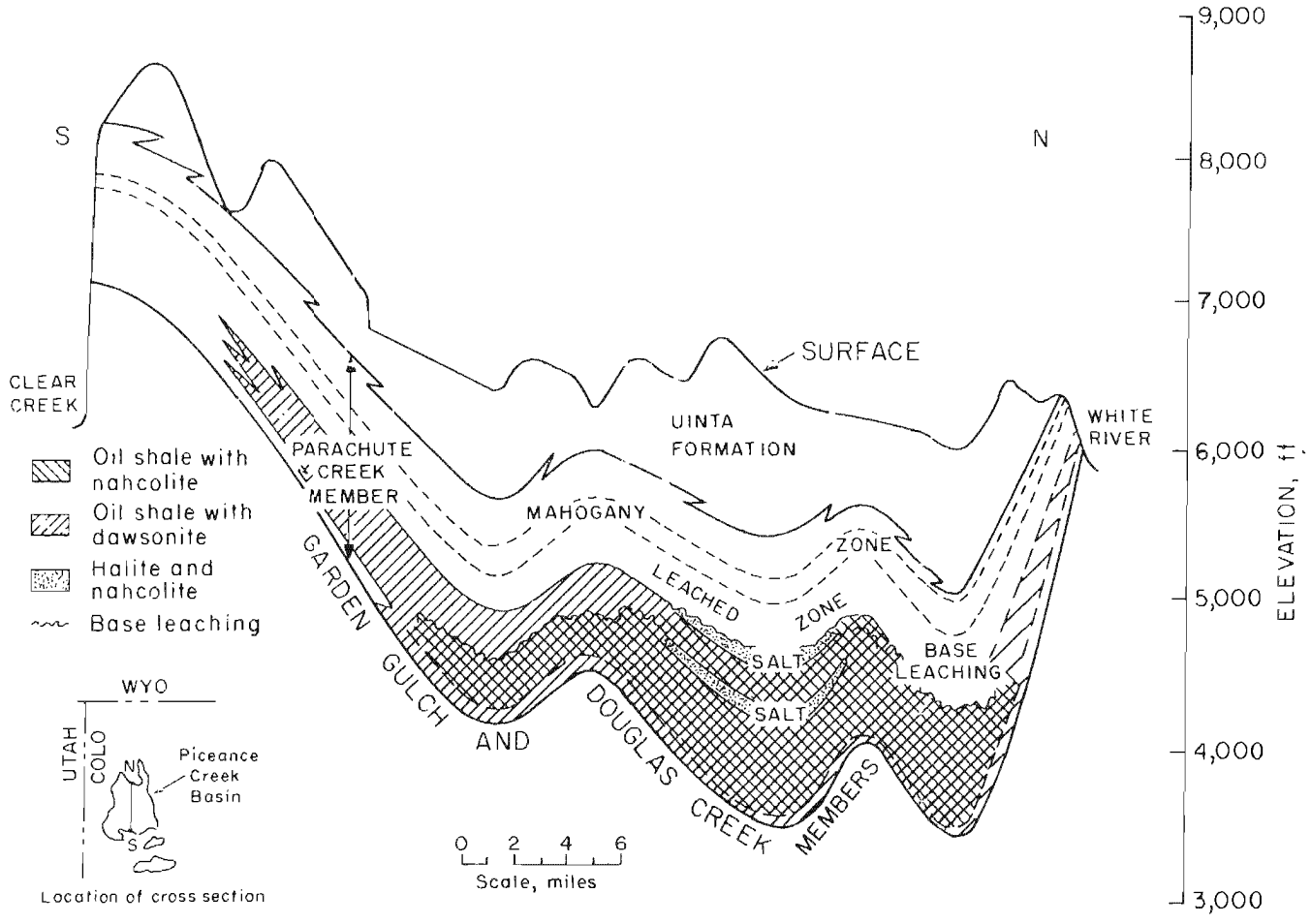

FIGURE 1. - South-north diagrammatic cross section of the Green River Formation in Colorado's Piceance Creek Basin (7).

The general procedure for extracting alumina from oil shale was described by Smith and Young (8). Raw shale is heated to produce shale oil, drive out the organic matter, and decompose the dawsonite to yield extractable alumina. When shale is heated to temperatures above 450° C, the organic matter (kerogen) decomposes to produce shale oil. The dawsonite decomposes below 400° C according to the reaction:

$$2NaAl(OH)_2CO_3 \rightarrow Al_2O_3 + Na_2CO_3 + CO_2 + 2H_2O.$$

Because about 90 pct of the original shale volume occupied by organic matter becomes void space, the spent shale is porous and easily broken into smaller pieces. The alumina released from the decomposition of dawsonite is easily extractable with dilute base. Both Smith (6) and Haas and Atwood (3) recommended that retorted shale be leached immediately and rapidly after retorting because some of the alumina will become insoluble in a weak base if exposed to moist air. Recovery of alumina from the leach liquor may be by precipitation of $Al_2O_3 \cdot 3H_2O$ upon addition of CO_2, or possibly by seeding to crystallize $AL_2O_3 \cdot 3H_2O$ from supersaturated solutions.

It appears that shale oil recovery is independent of shale particle size; 3- to 6-in feed material can be retorted to obtain the same oil recoveries as those for smaller sized shale. On the other hand, optimum extraction of alumina with dilute base is obtained on much smaller sized spent shale. The published literature contains data on caustic leaching of a variety of sizes of spent shale, but the optimum size for maximum extraction is not known.

Furthermore, because spent shale is very friable and raw shale is not, grinding costs would be lowered by grinding spent shale rather than raw shale. But grinding spent shale would result in a time lag between retorting and leaching (unless a grinding leach is successful), and it would be a departure from the recommendation for "immediate and rapid leaching" of spent shale. It also may not be practical for other reasons to leach spent shale "immediately." Therefore, it would be helpful to know more precisely the conditions under which spent shale may be safely stored prior to caustic leaching to avoid losses in alumina extraction, and also the magnitude of losses after storage under a variety of potential storage conditions.

Although Haas and Atwood (3) reported that SiO_2 dissolution could be reduced to result in less than 0.03 pct in alumina, there was a general lack of information on the extent of dissolution of other impurities in caustic leach liquor. Impurities should be kept low to avoid contamination of cell-grade alumina and, possibly, aluminum metal. The allowable levels of undesirable impurities in cell-grade alumina are about 0.025 pct SiO_2, 0.03 pct Fe_2O_3, 0 06 pct CaO, 0.005 pct TiO_2, and 0.001 pct P_2O_5 (10). Phosphorus reduces current efficiency during electrolysis of alumina in cryolite, and Si, Fe, and Ti reduce the electrical conductivity of aluminum metal.

This report describes the results of a preliminary investigation to determine the effects of particle size, retorting temperature, and spent shale storage conditions on (1) extraction of alumina and soda and (2) dissolution of the impurities such as Ca, Fe, Ti, Si, and P in caustic leach liquor.

MATERIALS

The dawsonite-bearing oil shale used in this study was part of a 100-ton lot mined from the 2,100-ft level of the Bureau of Mines borehole at Horse Draw in the Piceance Creek Basin. Samples of a 5-ton composite crushed to minus 1-1/2-in size were crushed to smaller sizes for use in this study. The 1-1/2-in raw shale was reduced to 1/4 in. in a jaw crusher and ground further to minus 8 mesh in a cone mill. Further size reductions were made in a hammer mill.

A Fischer assay for the crushed oil shale is shown in table 1, and chemical analyses are shown in table 2. The analyses in table 2 show that the raw shale contained about 12 pct dawsonite and essentially no nahcolite. The alumina extractable with hot HCl was equivalent to the dawsonite present. Contrary to observations by Smith (6), this shale did not contain detectable amounts of nordstrandite ($Al_2O_3 \cdot 3H_2O$), as indicated by chemical and X-ray diffraction analyses. Analysis of various size fractions of raw shale crushed to pass through an 8-mesh sieve showed that dawsonite was concentrated in the finest size fractions. X-ray diffraction analyses showed that the minus 270-mesh size fraction contained about 22 pct dawsonite compared with 12 pct in the bulk sample.

TABLE 1. - Fischer assay for oil shale

Screen size of sample, mesh	Yield of product						Specific gravity of oil at 60°/60° F	Tendency to coke
	wt-pct				gal/ton			
	Oil	Water	Spent shale	Gas + loss	Oil	Water		
8 by 10.....	13.3	1.7	78.0	7.0	35.6	4.1	0.898	Slight.
Minus 65.....	12.7	1.8	77.7	7.8	33.8	4.3	.901	None.

NOTE.--Assay made by Laramie Energy Technology Center, U.S. Department of Energy, Laramie, WY.

TABLE 2. Analysis of raw oil shale,[1] weight-percent

Component	A[2]	B	C	D
Al_2O_3		9.24	9.37	10.2
Na_2O		3.26	3.17	3.0
CaO		5.61	5.53	4.55
MgO		3.63	3.64	3.12
K_2O		1.94	2.01	1.84
Fe_2O_3		3.86	3.65	3.5- 4.5
SiO_2		36.8	37.0	35.2
P_2O_5		.53	.66	.24
TiO_2		.61	.53	.48
Water-soluble sodium	0.08			
Nahcolite[3]	.29			
HCl-soluble sodium	2.0		2.22	
Dawsonite[4]	12.0			
HCl-soluble Al_2O_3	4.2		4.80	
Al_2O_3 in dawsonite	4.3			
Excess Al_2O_3	-.1			
Nordstrandite[5]	.0			

[1]A, B, C, and D represent 4 different samples from a 5-ton composite from the 100-ton lot.

[2]Via method used by Smith and Young (8).

[3]Based on water-soluble sodium.

[4]Based on HCl-soluble sodium.

[5]Based on excess Al_2O_3.

NOTE.--Blank spaces indicate no data.

PROCEDURES

Raw shale was crushed, then retorted to obtain spent shale that was leached in dilute caustic to extract alumina and soda. All filtrates were analyzed for alumina and soda, and some were analyzed for the unwanted impurities: Ca, Si, Fe, P, and Ti. Preliminary tests were made to determine which factors had a significant effect on extraction and impurity dissolution. The factors included particle size, retorting temperature, leaching variables, and spent shale storage conditions.

Subsequent tests were made on shale retorted at 450° to 800° C to determine the effect of influential factors at several levels.

RETORTING

The crushed shale was heated in a 5-in-OD stainless steel tube, shown in figure 2, to drive out the shale oil and gaseous decomposition products. Retorting temperatures of 500° and 700° C were used for the preliminary experiments and ranged from 450° to 800° C in subsequent tests. A typical run consisted of the following sequence:

1. Flush out the system with nitrogen.

2. Heat to temperature in about 30 min in flowing nitrogen.

3. Hold at temperature for about 50 min.

4. Cool to less than 75° C under nitrogen flow.

Total run times ranged from 3 to 4 hr. The weight-percent of spent shale decreased with increasing retorting temperature as shown in figure 3.

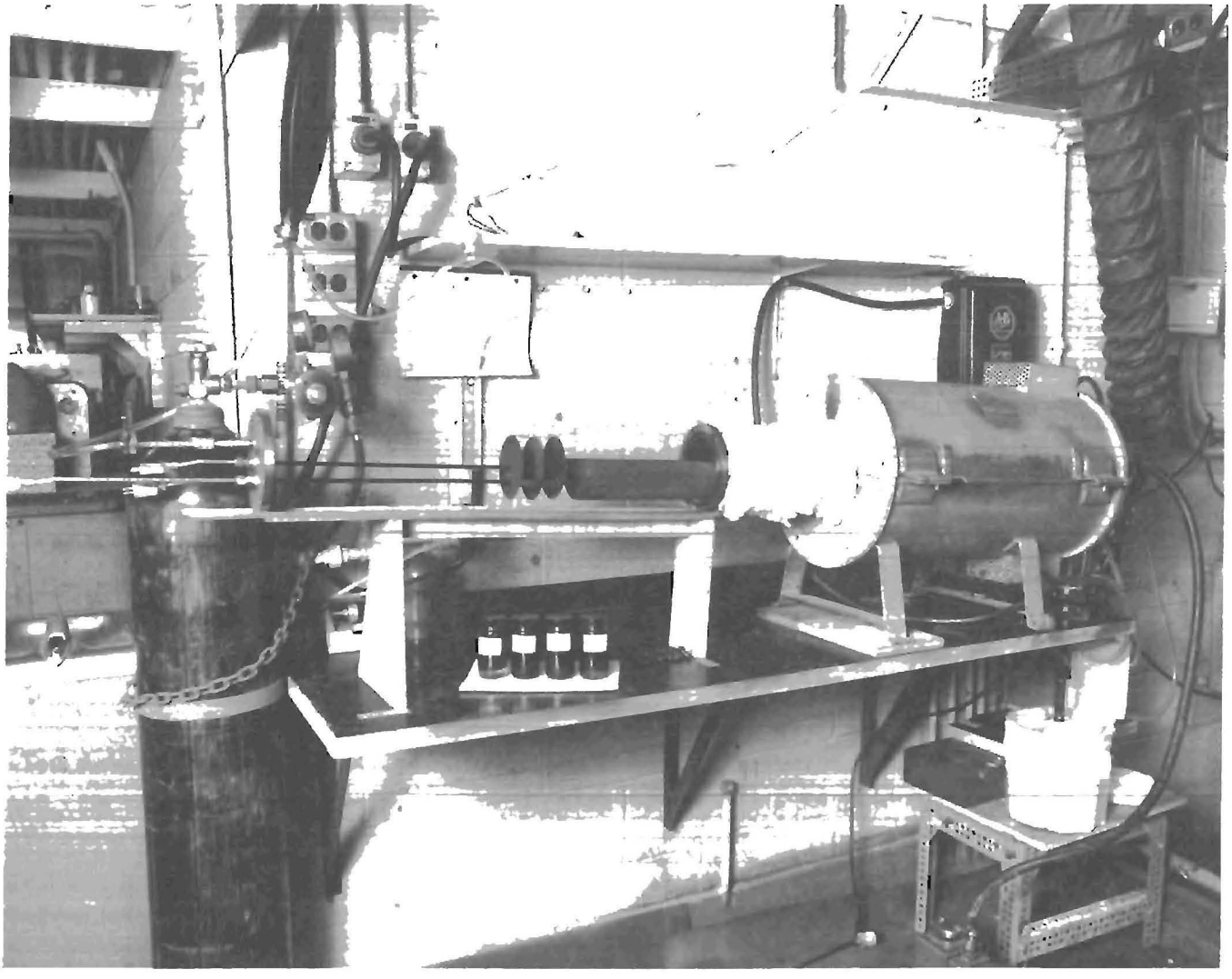

FIGURE 2. - Furnace assembly used to retort oil shale.

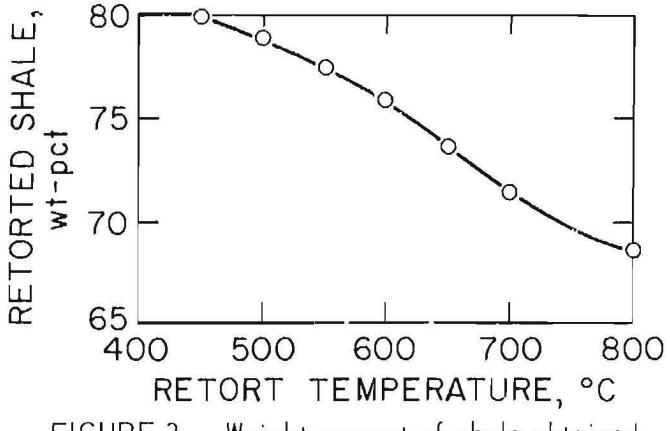

FIGURE 3. - Weight-percent of shale obtained by retorting raw shale at 450° to 800° C.

SPENT SHALE STORAGE

In the preliminary experiments, storage in nitrogen was obtained by evacuating one-pint mason jars in a glove box, backfilling with dry nitrogen, and capping. Constant relative humidities (RH) of 0 or 100 pct were maintained by storing spent shale in glass bottles in sealed mason jars containing a desiccant or water. The mason jars were stored in a refrigeration unit at 0°±1° C or in an oven at 40°±2° C. The samples stored for the preliminary tests were not stirred during the storage period.

After it was found that there was no significant difference whether the shale was stored in nitrogen or air, spent shale was stored in air at 0°±1° C, 21°±2° C, or 42°±2° C in subsequent experiments. In these later tests the samples with a bed depth of 1-1/2- to 1-in thickness were mixed manually after being stored for 1 day and were mixed once each week thereafter. During mixing, the shale was exposed to room air at 21° C and 50 to 60 pct RH for 2 to 3 min.

Solutions used to maintain constant relative humidities are listed in table 3.

TABLE 3. - Materials and solutions used to maintain constant relative humidities

Temp., °C	RH, pct	Material or saturated aqueous salt solution
0.....	0	$CaSO_4$ desiccant (Drierite).[1]
	25	$KC_2H_3O_2$ (potassium acetate).
	51	$K_2CO_3 \cdot 2H_2O$.
	76	NaCl.
	100	Water.
21....	23	$KC_2H_3O_2$ (potassium acetate).
	55	$Na_2Cr_2O_7 \cdot 2H_2O$.
	75	NaCl.
40....	0	$CaSO_4$ desiccant (Drierite).
	100	Water.
42....	20	$KC_2H_3O_2$ (potassium acetate).
	54	$Na_2Cr_2O_7 \cdot 2H_2O$.
	75	NaCl.

[1]Reference to specific brand names or manufacturers is for identification only and does not imply endorsement by the Bureau of Mines.

LEACHING

Unretorted shale was leached with boiling HCl to determine the amount of acid-extractable alumina and soda. Minus 65-mesh, 5-g samples were leached for 15 min in 150 mL of concentrated HCl diluted to 300 mL. After the solution was cooled to room temperature and filtered, the residue was washed with 800 mL of hot water. The filtrate was diluted to 1 L with distilled water and analyzed for alumina and soda. This method is similar to that used by Smith and Young (9). Percent extractions for alumina and soda from spent shale were based on considering the acid-extractable amounts in raw shale as 100 pct.

Retorted shale was leached with dilute NaOH to extract the alumina and soda. In most tests, spent shale samples obtained by retorting 25-g samples of raw shale were leached at room temperature (21° C) for 15 min in 80 mL of 0.5N NaOH. The solution was mechanically stirred during leaching. After filtering, the residue was washed with 350 mL of distilled water. The resultant filtrate was acidified with 200 mL of concentrated (37 wt-pct) HCl, then heated for an hour to agglomerate some high-sulfur precipitates. The cooled filtrate was diluted to 1 L and analyzed for alumina and soda.

Both Smith (6) and Haas and Atwood (3) recommended that retorted shale be leached immediately and rapidly. The importance of rapid leaching was also shown in this study in one series of leaching tests on shale of two particle sizes, retorted at 500° C in duplicate. One sample of each size was leached immediatly while being stirred in the normal manner. A second sample of each particle size was allowed to sit in stagnant 0.5N NaOH for about 35 min before stirring. The alumina extractions were about 10 pct lower for the samples allowed to sit in stagnant caustic.

RESULTS OF PRELIMINARY TESTS TO DETERMINE INFLUENTIAL FACTORS

Two preliminary experiments were made to determine the most influential factors on alumina and soda extraction and dissolution of impurities Ca, Si, Fe, P, and Ti. The factors considered at two levels in a 2^6 factorial design were--

1.	Retorting temperature	500°, 700° C
2.	Shale particle size	minus 8 plus 10, minus 65 mesh.
3.	NaOH concentration	0.3N, 1.0N.
4.	Leaching temperature	25°, 65° C.
5.	Leaching time	5, 30 min.
6.	Liquid-solid ratio	4, 10.
7.	Spent shale storage atmosphere	nitrogen, air.
8.	Spent shale storage temperature	0°, 40° C.
9.	Spent shale storage time	1, 4 weeks.
10.	Spent shale storage humidity	0, 100 pct RH.

Factors 1 through 6 were considered in experiment I, and factors 1, 2, 7, 8, 9, and 10 were studied in experiment II. Summaries of the statistical evaluation of results for both experiments are shown in tables 4 and 5. The relative effects of the factors on extraction are summarized in table 6.

For experiment I, the only significant factors were retorting temperature and particle size. Higher alumina and soda extractions were obtained for shale ground to pass through a 65-mesh sieve and retorted at 500° C. Caustic concentration, liquid-solid ratio, leaching temperature, and leaching time had no significant effects within the limits tested. None of the six factors had a significant effect on the dissolution of impurities Si, Fe, Ti, and P. Calcium dissolution was significantly lower for shale retorted at the lower temperature.

TABLE 4. - Summary of the statistical evaluation of results for preliminary experiments I and II

Extraction pct for[1]	Al_2O_3	Na_2O	CaO	SiO_2	P_2O_5	TiO_2
EXPERIMENT I (1/4 REPLICATE OF 2^6 FACTORIAL DESIGN)						
Mean	62.3	42.2	0.011	0.104	0.174	0.029
Estimated standard deviation	7.7	13.2	.005	.110	.44	.013
Coefficient:						
Retort temperature	-4.9	-28.4	.007	.017	.079	-.007
Particle size[2]	9.5	.5	.003	.011	.102	.003
NaOH concentration	3.8	1.2	.001	.047	.118	.000
Leach temperature	.2	2.6	.001	.030	-.129	-.003
Leach time	2.7	2.3	.000	.010	.109	-.003
Liquid-solid ratio	2.4	2.3	.000	.041	.093	.005
EXPERIMENT II (1/2 REPLICATE OF 2^6 FACTORIAL DESIGN)						
Mean	49.5	21.2	0.013	0.089	0.060	.035
Estimated standard deviation	16	13	.006	.018	.019	.023
Coefficient:						
Retort temperature	-1.3	-16.5	.008	.025	-.025	-.003
Particle size[2]	6.3	-2.3	.003	.004	-.002	-.007
Storage gas	-.5	.9	-.001	-.003	.006	-.003
Storage temperature	-11.8	.6	-.003	.024	-.000	.004
Storage time	-3.3	-4.8	-.000	.000	.000	.007
Relative humidity	-26.8	1.5	-.003	.032	.005	-.006

[1] Fe_2O_3 dissolution low, and <0.002 for all but 2 factors, retorting temperature and leaching temperature.

[2] Coarse to fine, all others low to high.

TABLE 5. - Abbreviated analyses of variance for preliminary experiments I and II

Source	d.f.[1]	Mean squares					
		Al_2O_3	Na_2O	CaO x 10^{-6}	SiO_2 x 10^{-6}	P_2O_5 x 10^{-6}	TiO_2 x 10^{-6}
EXPERIMENT I (1/4 REPLICATE OF 2^6 FACTORIAL DESIGN)[2]							
Retort temperature	1	381*	12,877*	827*	4,761	0.1006	870
Particle size[3]	1	1,434*	5	138	1,806	.1671	130
NaOH concentration	1	233	23	5	35,156	.2218	0
Leach temperature	1	0	112	28	14,042	.2673	140
Leach time	1	115	84	2	1,640	.1894	160
Liquid-solid ratio	1	95	85	0	26,978	1888	220
Residual	9	59	174	24	12,202	.1940	180
Critical variance for 95 pct confidence	NAp	302	891	123	62,474	.99	920
EXPERIMENT II (1/2 REPLICATE OF 2^6 FACTORIAL DESIGN)[2]							
Retort temperature	1	51	8,705*	2,228*	20,000*	20,050*	205
Particle size[3]	1	1,286*	166	270*	561	140	1,391
Storage gas	1	7	24	20	242	1,047	358
Storage temperature	1	4,496*	11	226*	18,915*	0	639
Storage time	1	341	724*	3	1	3	1,445
Relative humidity	1	22,903*	68	259*	33,025*	790	1,116
Residual	23	252	167	36	3,271	351	542
Critical variance for 95 pct confidence	NAp	1,079	715	154	14,000	1,052	2,320

*Significant effect at 95 pct confidence. NAp Not applicable. [1]Degrees of freedom.
[2]Fe_2O_3 dissolution low, and <0.002 pct for all factors.
[3]Coarse to fine, all others low to high.

TABLE 6. - Relative effect of factors on extraction in preliminary experiments I and II

Factor	Experiment	Effect of factor on--						
		Extraction of--		Dissolution of--				
		Al_2O_3	Na_2O	Ca	Si	P	Ti	Fe
Retort temperature	I	Slight	Great	Great	None	None	None	None
Do	II	None	Great	Great	Slight	Great	None	None
Particle size	I	Great	None	None	None	None	None	None
Do	II	Slight	None	Slight	None	None	None	None
Leaching:								
NaOH concentration	I	None	None	None	None	None	None	None
Temperature	I	None	None	None	None	None	None	None
Time	I	None	None	None	None	None	None	None
Liquid-solid ratio	I	None	None	None	None	None	None	None
Storage:								
Gas	II	None	None	None	None	None	None	None
Temperature	II	Great	None	Slight	Great	None	None	None
Time	II	None	Slight	None	None	None	None	None
Relative humidity	II	Great	None	Slight	Great	None	None	None

General effects:

Retort temperatures	Increasing temperature	Decreased Na_2O extraction. Increased Ca dissolution. Increased P dissolution.[1]
Particle size	Increasing particle size	Decreased Al_2O_3 extraction.
Storage temperature	Increasing temperature	Decreased Al_2O_3 extraction. Decreased Ca dissolution. Increased Si dissolution.
Storage time	Increasing time	Decreased Na_2O extraction.
Storage humidity	Increasing humidity	Decreased Al_2O_3 extraction. Increased Si dissolution.

[1]P showed increase in experiment II but not in experiment I.

For experiment II, particle size, retorting temperature, and all of the spent shale storage factors except storage atmosphere had a significant effect. Storage in nitrogen or air made no significant difference. The more significant effects from experiment II were—

1. Alumina extraction was greatly reduced when the finer sized shale was stored in warm, moist air.

2. Soda extraction was lower for shale retorted at the higher temperature.

3. The dissolution of impurities Ca and Si was variously affected by retorting temperature, storage temperature, and storage humidity, as shown in table 6.

4. The dissolution of impurities Ti and Fe was low and not affected by any factors.

Since experiment I showed no effects from the four leaching factors, subsequent extractions were made by leaching for 15 min with 0.5N NaOH at room temperature at a liquid-solid ratio of 4.

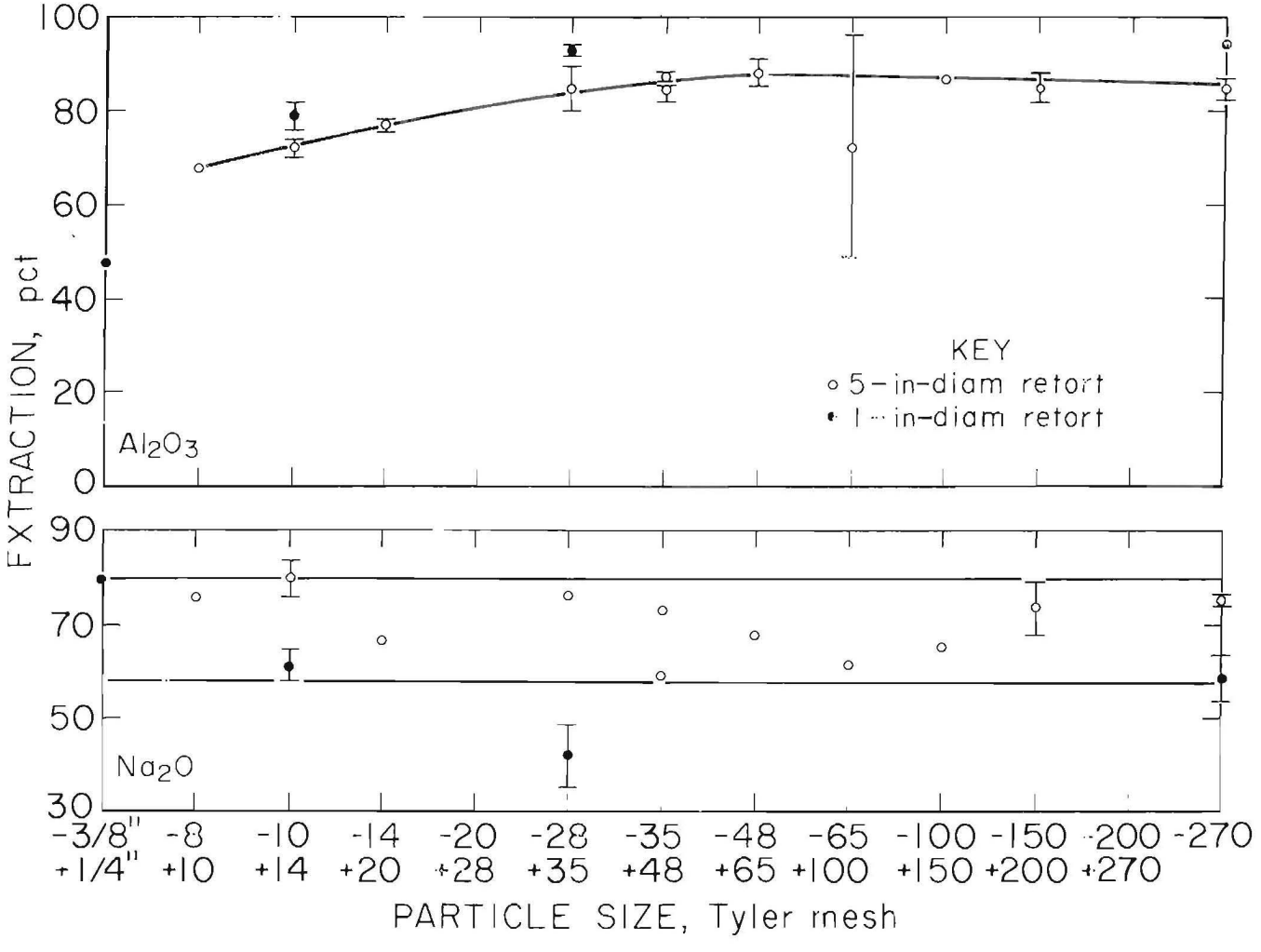

FIGURE 4. - Effect of particle size on alumina and soda extraction with 0.5N NaOH for shale retorted at 500° to 550° C. Soda extraction was not affected by particle size. The parallel lines in the lower graph mark the boundaries of a band within which soda extractions ranged.

RESULTS OF SUBSEQUENT EXPERIMENTS

Based upon the results of the preliminary experiments, subsequent tests were made to determine in greater detail the effects of particle size, retorting temperature, and spent shale storage temperature and humidity on extraction of alumina and soda and on dissolution of impurities.

EFFECT OF PARTICLE SIZE ON ALUMINA AND SODA EXTRACTION

The effect of particle size on alumina and soda extraction is shown graphically in figure 4. These results for shale retorted at 500° to 550° C showed that shale size should be 28 mesh or finer to obtain maximum alumina extraction. Soda extraction was independent of particle size.

EFFECT OF RETORTING TEMPERATURE ON ALUMINA AND SODA EXTRACTION

The effect of retorting temperature on alumina and soda extraction is summarized in table 7 and shown graphically in figure 5. The results obtained for shale retorted in the 5-in-diam retort showed that alumina extraction was highest and independent of retorting temperatures between 450° and 650° C. Alumina extraction was slightly lowered for shale retorted at 700° C and greatly lowered for shale retorted at 800° C. Soda extractions decreased with increase in retorting temperature.

The results obtained for the 1-in-diam retort did not agree with those obtained for the 5-in retort. Alumina extraction was definitely lowered and soda extraction was reduced to zero for shale retorted at 650° C, as shown in figure 5. The results for shale retorted in the 1-in retort agree more closely with that reported in the literature. Because it was possible to control temperature more closely in the 1-in retort, these results are probably more reliable. They indicated that shale should be retorted below 600° C to obtain maximum alumina extraction.

TABLE 7. - Effect of retorting temperature on alumina and soda extraction for 28-mesh shale and finer

Retort temp., °C	Shale size, Tyler mesh	Number of tests	Extraction, pct	
			Al_2O_3	Na_2O
5-in retort:				
500	Minus 35..	9	86.1± 1.9	73.5± 3.9
600	...do.....	7	86.1± 1.7	33.2± 8.1
700	...do.....	7	79.2± 2.4	10.7± 9.4
800	...do.....	9	26.0±11.6	.0
450	Minus 28..	6	85.2± 9.1	80 ±33
550	...do.....	6	86.2± 3.5	68 ±29
650	...do.....	5	86.1± 4.2	42 ±30
1-in retort:				
525	Minus 270.	2	94.6± .2	58.5± 4.7
550	Minus 28..	4	95.8± 5.0	51.9±20
650	Minus 48..	4	78.5± 6.6	.0

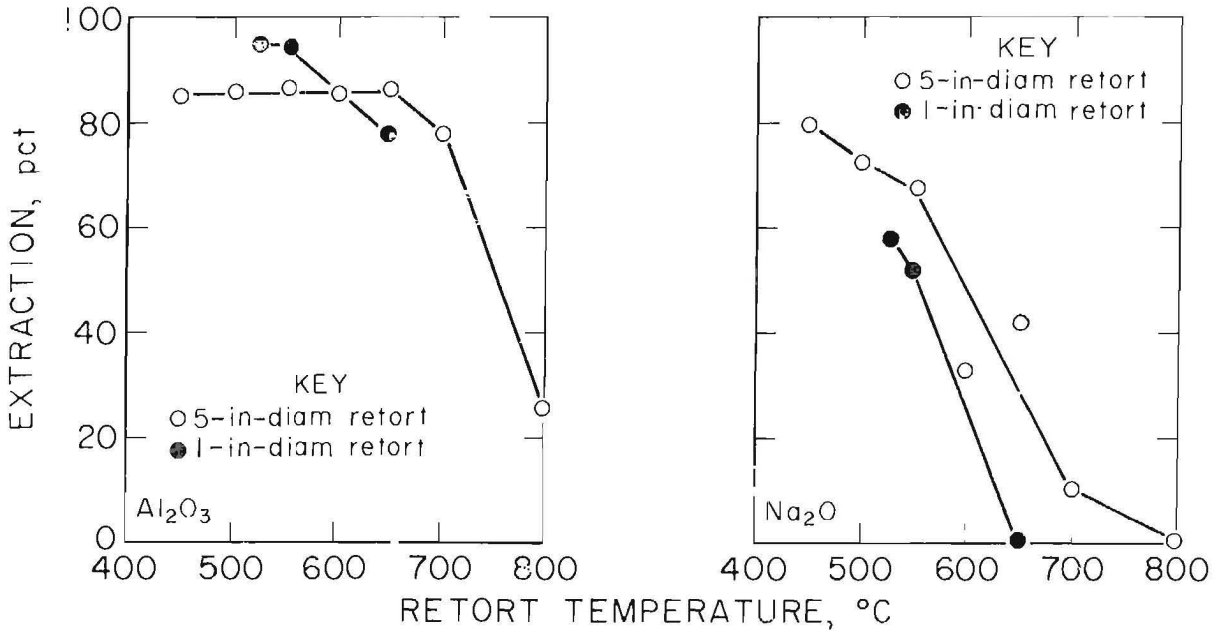

FIGURE 5. - Effect of retorting temperature on alumina and soda extraction with 0.5N NaOH at room temperature.

EFFECT OF RETORTING TEMPERATURE ON DISSOLUTION OF IMPURITIES Ca, Si, P, Ti, AND Fe

The effect of retorting temperature on dissolution of impurities, shown in table 8, indicated that CaO dissolution increased slightly with increased temperature. Silicon dioxide dissolution was lowest for shale retorted at 700° C.

EFFECTS OF SPENT SHALE STORAGE CONDITIONS ON ALUMINA AND SODA EXTRACTION

Brief Exposure to Room Air

One series of tests was made to determine the effect of exposing spent shale to room air for periods of less than 1 hr. Shale ground to pass through a 65-mesh sieve was retorted at 500° C, exposed to room air at 26° C and 50 pct RH for 5 or 45 min, and then stored in dry air ($CaSO_4$, desiccant) at room temperature for periods of up to 72 hr. The results of three leaching tests (three samples stored for a common period of time, one from each of three retorting runs) were averaged to obtain the results listed in table 9. Alumina and soda extractions were generally independent of exposure times and subsequent storage time. However, they were slightly higher and more consistent for retorted shale exposed to room air for 5 min than for shale exposed for 45 min.

TABLE 8. - Dissolution of impurities in 0.5N NaOH for shale retorted at various temperatures

(Filtrate analysis, grams per liter)

Retort temp., °C	Al_2O_3	CaO	SiO_2	P_2O_5	TiO_2	Fe_2O_3	MgO
500	12.3	0.075	0.087	0.075	0.012	0.012	ND
	9.9	.112	.063	.087	.024	.012	ND
700	9.6	.300	.025	.024	.012	.012	ND
	8.6	.175	.012	.012	.012	.012	ND
800	4.75	.438	.050	.012	.012	.002	0.001
	3.80	.438	.050	.012	.024	.002	.001

ND Not determined.

TABLE 9. - Effect of brief exposure of spent shale to room air on alumina and soda extraction

Storage time, hr	5-min exposure before storage[1]	45-min exposure before storage[1]
	Al_2O_3, pct[2]	
0.....	89.8±1.6	86.0±4.9
8.....	90.0±2.7	86.4±5.9
24.....	89.9±1.8	87.5±4.6
72.....	91.3±3.7	91.1±1.6
Mean.	90.2±2.5	87.8±4.2
	Na_2O EXTRACTION, pct[2]	
0.....	59.0±3.3	54.4±2.1
8.....	62.2±.1	57.9±3.6
24.....	59.2±3.2	54.6±2.5
72.....	60.2±2.4	55.9±3.2
Mean.	60.1±2.3	55.7±2.9

[1]Spent shale exposed to room air at 26° C with 50 pct RH.

[2]Data are averages of tests on samples from each of 3 retorting runs. R-19, 20, 21.

Storage Humidity, Temperature, and Time

To determine the effects of spent shale storage conditions on alumina and soda extraction with 0.5N NaOH for shale retorted at 500° C, a series of 25-g samples of minus 28-mesh shale were retorted. Two samples from each of four retort runs were leached within a few hours after retorting. The remaining samples were stored for 2, 5, 12, and 30 days at 0°, 21°, and 42° C at approximately 20, 50, and 75 pct RH, before leaching. The filtrate from the leachings was analyzed for alumina and soda. The test series for the stored samples consisted of an original set of 36 tests and a duplicate set. A different combination of storage temperature, relative humidity, and storage time was used for each test.

Results for the eight samples leached without storage, listed in table 10, showed that the alumina and soda extractions for retorted shale before storage were 88.3±2.2 pct and 67.5±4.3 pct, respectively. The alumina and soda extractions for the samples leached after storage are listed in tables 11, 12, and 13, and the mean results are shown graphically in figures 6 and 7. Alumina and soda extractions for shale stored for 12 days at 21° C and 23 pct RH showed wide variations, as shown in the center graphs of figure 6. There was no apparent explanation for this discrepancy.

TABLE 10. - Alumina and soda extraction for retorted shale before storage

Retort run	Leach run	Extraction, pct	
		Al_2O_3	Na_2O
R-50.....	210	86.7	64.0
	220	88.3	73.3
R-51.....	250	90.8	70.7
	260	86.7	66.7
R-52.....	190	88.3	68.0
	200	85.0	61.3
R-53.....	230	91.7	72.0
	240	89.2	64.0
Mean.....	NAp	88.3	67.5
Stnd. dev.....	NAp	2.2	4.3

NAp Not applicable.

TABLE 11. - Effect of storage time and relative humidity on alumina and soda extraction for shale retorted at 500° C and stored at 0° C, percent[1]

Storage time, days	Al_2O_3			Na_2O		
	A[2]	B	Mean	A	B	Mean
25 pct RH:						
0.....	([3])	([3])	88.3	([3])	([3])	67.5
2.....	88.3	90.8	89.6	73.3	74.7	74.0
5.....	85.8	86.7	86.2	70.7	77.3	74.0
12.....	88.3	85.5	86.7	77.3	68.0	72.7
30.....	84.2	87.5	85.0	74.7	73.3	74.0
51 pct RH:						
0.....	([3])	([3])	88.3	([3])	([3])	67.5
2.....	89.2	90.0	89.6	72.0	72.0	72.0
5.....	83.3	85.0	84.2	70.7	76.0	73.3
12.....	82.5	79.2	80.8	69.3	70.7	70.0
30.....	56.7	56.7	56.7	69.3	76.0	72.7
76 pct RH:						
0.....	([3])	([3])	88.3	([3])	([3])	67.5
2.....	88.3	89.2	88.8	66.7	68.0	67.3
5.....	82.5	70.0	76.3	68.0	70.7	69.3
12.....	60.8	39.2	50.4	73.3	69.3	71.9
30.....	15.8	15.0	15.4	73.3	68.0	70.6

[1]Based on acid extractables of 4.8 pct Al_2O_3 and 3 pct Na_2O.

[2]A and B represent 2 different samples.

[3]See table 10 for extraction before storage.

TABLE 12. - Effect of storage time and relative humidity on alumina and soda extraction for shale retorted at 500° C and stored at 21° C, percent[1]

Storage	Al_2O_3			Na_2O		
time, days	A[2]	B	Mean	A	B	Mean
23 pct RH:						
0.....	([3])	([3])	88.3	([3])	([3])	67.5
2.....	86.7	86.7	86.7	66.7	73.3	70.0
5.....	53.3	55.0	56.9	62.7	68.0	65.7
12.....	85.0	54.7	69.2	76.0	85.3	80.3
30.....	65.0	82.5	73.9	69.3	74.7	70.0
55 pct RH:						
0.....	([3])	([3])	88.3	([3])	([3])	67.5
2.....	90.0	88.3	89.2	65.3	65.3	65.3
5.....	67.5	57.5	62.5	65.3	73.3	69.3
12.....	37.5	29.2	33.3	69.3	68.0	68.7
30.....	9.2	9.2	9.2	73.3	74.7	74.0
75 pct RH:						
0.....	([3])	([3])	88.3	([3])	([3])	67.5
2.....	84.2	84.2	84.2	69.3	70.7	70.0
5.....	50.3	46.7	48.5	60.0	72.0	66.0
12.....	14.2	10.8	12.5	68.0	65.3	66.7
30.....	3.3	5.0	4.2	44.0	81.3	66.7

[1]Based on acid extractables of 4.8 pct Al_2O_3 and 3 pct Na_2O.

[2]A and B represent 2 different samples.

[3]See table 10 for extraction before storage.

TABLE 13. - Effect of storage time and relative humidity on alumina and soda extraction for shale retorted at 500° C and stored at 42° C, percent[1]

Storage	Al_2O_3			Na_2O		
time, days	A[2]	B	Mean	A	B	Mean
20 pct RH:						
0.....	([3])	([3])	88.3	([3])	([3])	67.5
2.....	89.2	90.8	90.0	70.7	65.3	68.0
5.....	83.3	85.0	84.2	66.7	72.0	69.3
12.....	82.5	80.0	81.3	69.3	66.7	68.0
30.....	81.7	80.8	81.3	77.3	78.7	78.0
54 pct RH:						
0.....	([3])	([3])	88.3	([3])	([3])	67.5
2.....	67.5	68.3	67.9	69.3	74.7	72.0
5.....	29.2	30.8	30.0	69.3	69.3	69.3
12.....	11.2	8.7	10.0	72.3	62.7	67.5
30.....	4.2	2.5	3.4	74.7	72.0	73.3
75 pct RH:						
0.....	([3])	([3])	88.3	([3])	([3])	67.5
2.....	48.3	45.8	47.1	72 0	73.3	72.7
5.....	10.0	11.7	10.8	70.7	66.7	68.7
12.....	3.7	3.6	3.6	78.7	69.3	74.0
30.....	1.7	1.7	1.7	69.3	82.7	76.0

[1]Based on acid extractables of 4.8 pct Al_2O_3 and 3 pct Na_2O.

[2]A and B represent 2 different samples.

[3]See table 10 for extraction before storage.

As seen in figure 6, soda extraction was independent of all storage conditions. The mean value for all 72 stored samples was 70.7±5.6 pct, compared with 67.5±4.3 pct for the 8 samples without storage. That soda extractions were independent of storage conditions suggests that soda was not associated with the alumina that became insoluble during storage.

Alumina extraction decreased with increased relative humidity (fig. 6). There was a big decrease in alumina extraction when the relative humidity was increased from 25 to 50 pct. Since no tests were made on shale stored in air between 25 and 50 pct RH, there could be a threshold relative humidity above 25 pct but below 50 pct that has a negligible effect on alumina extraction. The decrease in alumina extraction with an increase in relative humidity was accentuated by increased temperature.

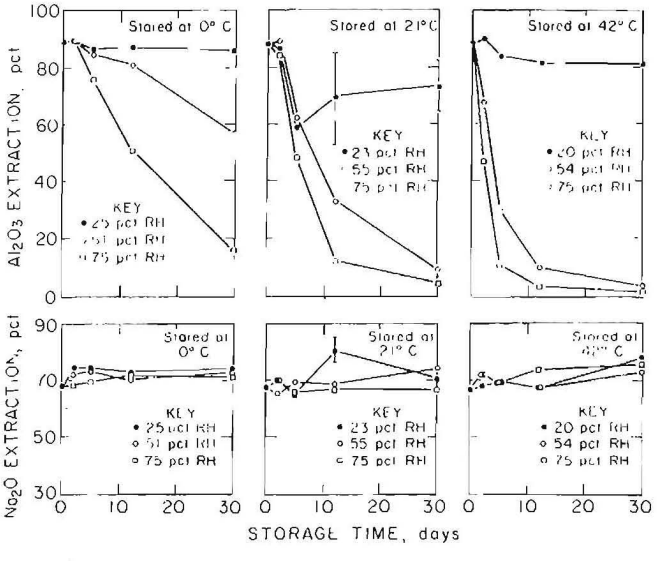

FIGURE 6. - Effect of storage time and relative humidity on alumina and soda extraction for shale retorted at 500° C, stored at 0°, 21°, and 42° C, and leached with 0.5N NaOH at 21° C.

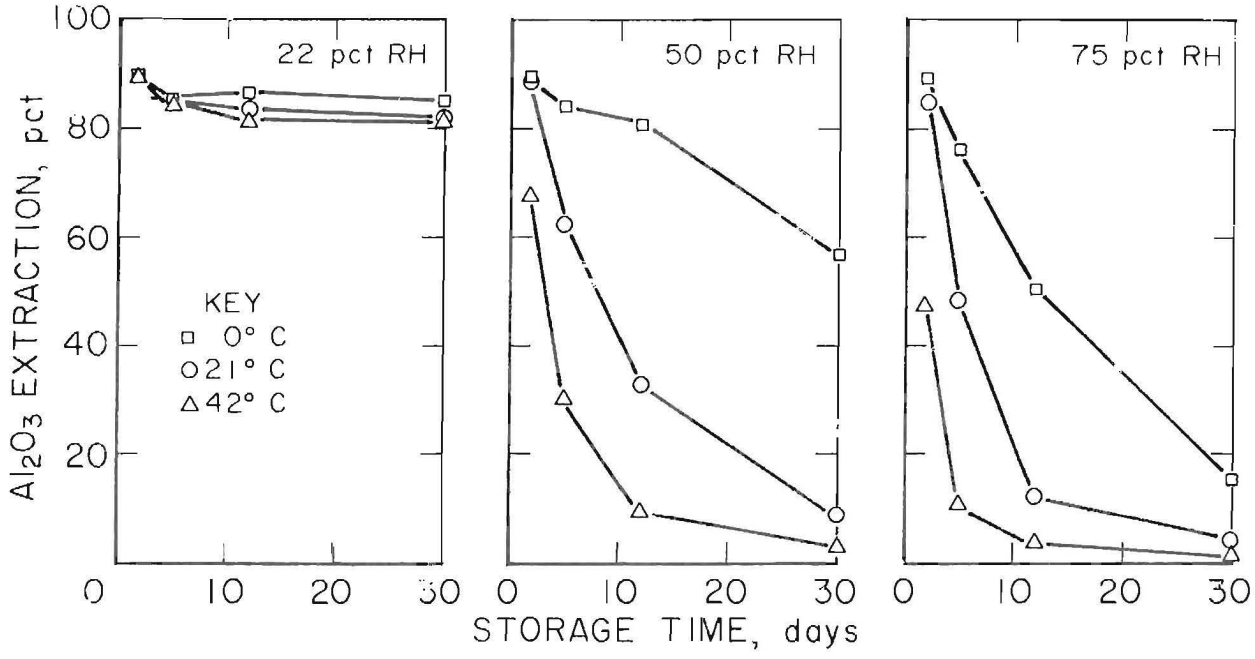

FIGURE 7. Effect of storage time, temperature, and relative humidity on alumina extraction for shale retorted at 500° C and leached with 0.5N NaOH at 21° C.

Some of the data in figure 6 were replotted in figure 7. The results indicated that alumina extraction for shale stored in air at 20 to 25 pct RH was independent of storage temperature and storage time. However, for samples stored at 50 and 75 pct RH, alumina extraction was greatly lowered with increased storage temperature and storage time.

DISCUSSION OF RESULTS

Significant variations in alumina concentration were observed in the different size fractions of crushed raw shale. This is because extractable alumina originates from dawsonite, which was found to be concentrated in the finer size fractions of crushed raw shale.

Shale retorted at 500° to 550° C in a 5-in-diam retort was leached to obtain maximum extractions of 90 pct Al_2O_3 and 70 pct Na_2O. These alumina extractions were lower than the extractions of greater than 100 pct reported by Haas and Atwood (3). Some of this difference may be due to the presence of moisture in the 5-in retort during cooling, which could reduce the amount of extractable alumina in the shale. This possibility was based on observations made in the earliest retorting tests, together with the results for shale retorted in a 1-in-diam retort. For shale retorted in the 1-in retort, in which dry conditions were obtained and maintained during cooling, alumina extraction was 90 to 95 pct (table 7).

PARTICLE SIZE

Tests made on narrow size fractions of shale ranging from 3/8 in to minus 270 mesh showed that particle size had no effect on soda extraction and dissolution of impurities, but had a significant effect on alumina extraction. Maximum alumina extractions were obtained on shale finer than about 28 mesh. For particles larger than 28 mesh, alumina extraction decreased linearly from 88 pct for minus 28-mesh shale to 68 pct for minus 8- plus 10-mesh shale. Because of the porous nature of retorted shale, such lowering of extraction with increase in

particle size might not be expected. A possible explanation could be related to the fact that maximum extractions are obtained by prompt and rapid leaching. When larger size particles are leached, the leachant may not be able to penetrate and leach coarser particles as rapidly as moisture (in the form of vapor or reagent-depleted liquid) penetrates and reacts to inactivate the alumina in the interior of the particles. The lowering in alumina extraction observed for shale allowed to sit in stagnant NaOH before stirring seems pertinent to this explanation.

RETORTING TEMPERATURE

Maximum alumina extractions for shale retorted in the 5-in retort were for a temperature range of 450° to 650° C. However, for shale retorted in the 1-in retort, maximum alumina extractions were obtained for shale retorted at or below 550° C, but not for shale retorted at 650° C (fig. 5). Results obtained for the 1-in retort were compatible with those reported by Smith and Young (9), who recommended that dawsonite-bearing shale should not be retorted above 550° C. Smith and Young believed that retorting shale above 600° C lowered alumina extraction because of the formation of insoluble alumina-containing glasses. The discrepancy in alumina extraction for shale from the 5- and 1-in retorts suggested that the effective temperature within the mass of the sample in the 5-in retort may have been as much as 50° C lower than the indicated temperature. Although the thermocouple used to monitor the shale temperature was located in the center of the shale charge in accord with temperature calibration runs, it is possible that the 50-min hold times may have been insufficient for the entire shale charge to attain a uniform temperature.

Soda extraction decreased very sharply with increased retorting temperature. The decrease in caustic-soluble soda for shale retorted above 600° C has been attributed to the reaction of Na_2CO_3 to form glassy silicates. However, there was no apparent explanation for the decrease in soda extraction for shale retorted between 450° and 600° C.

Dissolution of Fe, Ti, and P in 0.5N NaOH at room temperature was low and not affected by retorting temperature (table 8). Dissolution of SiO_2 was slightly affected by retorting temperature; the lowest amount was for shale retorted at 700° C and the highest for shale retorted at 500° C Because all leaching was done in glass vessels, the SiO_2 dissolutions could be high. Dissolution of calcium was increased with increase in retorting temperature.

RETORTED SHALE STORAGE CONDITIONS

The effect of added exposure of shale to moist room air during periodic mixing could be of concern. If the added exposure were significant, it would have affected the samples stored at 0° C. However, the high extractions for samples stored for 30 days at 0° C and 25 pct RH indicated that these results were reasonable and not affected by short-time exposure to room air during periodic mixing.

A good correlation was obtained between log alumina extraction and storage time and relative humidity for spent shale stored at 0° C. The equation for the best fit curve was

$$\ln y = 4.388 + 0.0345D + 0.00327H - 0.00121(D)(H),$$

in which $y = Al_2O_3$ extraction, in pct;

D = Storage time, in days;

H = Storage relative humidity, in pct.

Similar treatments of extraction data for shale stored at 21° C and 42° C did not yield as good a fit as the 0° C data, but the results of these correlations were used to estimate the maximum relative humidities at 88 pct Al_2O_3 extraction. These best fit relative humidity values

TABLE 14. - Estimated maximum humidites to obtain maximum alumina extraction of 88 pct for spent shale stored for 2 and 30 days at 0°, 21°, and 42° C

Storage temp., °C	Storage time, days	Maximum pct RH during storage to maintain maximum Al_2O_3 extraction of 88 pct	
		From best fit[1]	From experimental data[2]
0.....	2	50	>76
	30	28	>25, <51
21.....	2	30	30
	30	20	<23
42.....	2	25	>20, <54
	30	16	<20

[1]From best fit curves of log Al_2O_3 extraction versus storage time and humidity.

[2]From tables 11, 12, and 13.

are listed in table 14 and compared with experimental data to show fairly good agreement. These best fit values indicated that spent shale could be stored for 30 days without significant losses in alumina extraction if shale were stored at less than 28 pct, 20 pct, and 16 pct RH at 0°, 21°, and 42° C, respectively.

Humidity control could be a problem if proper precautions are not taken when spent shale stored at ambient temperature undergoes natural fluctuations in temperature during the course of a 24-hr day. Winter and summer temperature extremes in 1980 in Grand Junction, CO, occurred in January and July:

January.... 14° F (-10° C) at 75 pct RH.
51° F (10° C) at 80 pct RH.

July..... 56° F (13° C) at 48 pct RH.
100° F (38° C) at 21 pct RH.

In summer, if retorted shale were stored at ambient temperature during the heat of the day at 38° C and 21 pct RH, then allowed to cool to 20° C at night, the

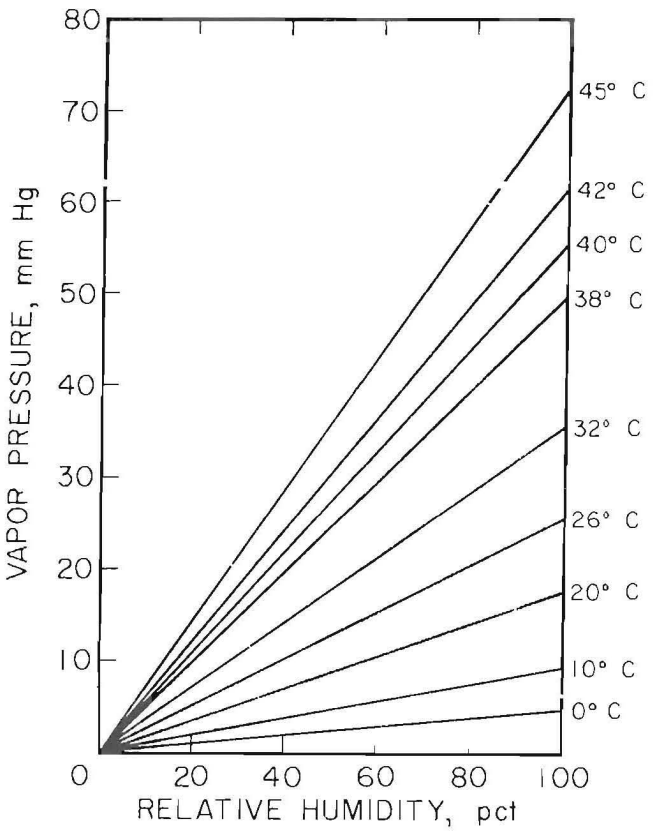

FIGURE 8. - Vapor pressure of water at various temperatures and relative humidities.

stagnant air at 20° C would have a relative humidity of 59 pct (fig. 8). On a winter day, if shale stored at 10° C and 80 pct RH were allowed to cool to 6° C, it would be below its dewpoint. This suggests that spent shale could not be stored in the open air without a good probability of sacrificing significant alumina extraction. It is possible that spent shale stored in big piles would be less subject to the action of humidity.

The optimum storage temperature would be one that could be most easily kept constant to avoid fluctuations in relative humidity. Storage of spent shale at 20° to 25° C in air with less than 20 pct RH would be a convenient storage condition for shale destined for subsequent caustic extractions at 25° C.

SUMMARY AND CONCLUSIONS

Crushed shale retorted at 450° to 800° C to obtain spent shale was leached in dilute NaOH to determine the effect of particle size, retorting temperature, leaching variables, and spent shale storage conditions on extraction of alumina and soda and dissolution of Ca, Si, Fe, Ti, and P.

The findings were in general agreement with those reported in the literature. The factors that had significant influence on alumina and soda extraction were retorting temperature, particle size, and spent shale storage conditions (relative humidity, temperature, and time):

Increasing retort temperature.....	Decreased Al_2O_3 extraction (above 650° C).
	Decreased Na_2O extraction.
	Increased Ca dissolution.
Increasing particle size.....	Decreased Al_2O_3 extraction.
Increasing storage temperature.....	Decreased Al_2O_3 extraction.
	Decreased Ca dissolution.
	Increased Si dissolution.
Increasing storage time.....	Decreased Na_2O extraction.
Increasing storage humidity.....	Decreased Al_2O_3 extraction.
	Increased Si dissolution.

Tests made on shale retorted at 450° to 800° C showed that increasing retorting temperature had a great effect on lowering soda and alumina extraction and a slight effect, if any, on the dissolution of impurities. Maximum soda extraction was obtained for shale retorted at the lowest temperatures. Maximum alumina extractions were obtained for shale retorted at temperatures below 600° C. Alumina extractions for shale retorted at 650° C and 800° C were 80 pct and 26 pct, respectively. Dissolution of Fe, Ti, and P was low and not affected by retorting temperature.

Variations in particle size had no effect on soda extraction and dissolution of impurities. Alumina extraction decreased for particles larger than 28 mesh, from 88 pct for minus 28-mesh shale to 68 pct for minus 8- plus 10-mesh shale.

A comparison of the effects of the following levels of leaching factors showed that varying the levels had no significant effect on extraction of alumina and soda and dissolution of impurites Ca, Si, Fe, Ti, and P:

1. NaOH concentrations of 0.3N and 1.0N.

2. Leaching temperatures of 25° and 65° C.

3. Leaching times of 5 and 30 min.

4. Liquid-solid ratios of 4 and 10.

Leaching tests made on retorted shale stored for periods of up to 30 days at various temperatures and relative humidities showed that--

1. Alumina and soda extraction and dissolution of impurities were the same for shale stored in nitrogen or air.

2. Alumina extraction was lowered by increased storage temperature, storage humidity, and storage time.

3. Dissolution of P, Ti, and Fe was unaffected, but dissolution of Ca and Si was affected by storage temperature and humidity.

The raw shale used in this work yielded 13 pct oil (35 gal/ton) and contained 12 pct dawsonite. Approximately all of the HCl-soluble alumina and soda was contained in dawsonite. Of the 9 to 10 pct total Al_2O_3 and 3 pct Na_2O equivalents present in raw shale, 4.5 to 5 pct Al_2O_3 and 2.8 pct Na_2O were extractable with hot HCl. Portions of the alumina and soda that were insoluble in hot HCl are believed to be tied up as sodium and potassium feldspars and illite clay (5). None of these minerals are decomposed when retorted to yield caustic-soluble alumina and soda. The caustic-soluble alumina and soda are approximately equivalent to the amount released by the decomposition of dawsonite when retorted. Caustic extraction percentages were based on considering the acid-extractable values as 100 pct. Approximately 90 pct and 70 pct of the acid-extractable alumina and soda, respectively, were extractable with weak caustic. Of the 9 to 10 pct total Al_2O_3 and 3 pct total Na_2O equivalents present in raw shale, then, 4.05 to 4.5 pct Al_2O_3 and 2 pct Na_2O were extracted from the spent shale with caustic.

This investigation showed that maximum alumina and soda extractions were obtained by a 0.5N NaOH leach of minus 28-mesh spent shale obtained by retorting dawsonite-bearing oil shale at about 500° C, the lowest temperature compatible with optimum oil recovery.

Dawsonite-bearing oil shale retorted at 500° C can be leached with 0.5N NaOH to routinely extract about 90 pct of the acid-extractable soda. Although they may be difficult to achieve on a practical basis, alumina extractions greater than 95 pct seem probable if spent shale is not exposed to moisture and is leached at a rapid rate.

If spent shale can be stored in relatively dry air, alumina extractions of 90 pct can be maintained. The maximum relative humidities for suitable storage were estimated to be 28, 20, and 16 pct at storage temperatures of 0°, 21°, and 42° C, respectively. These humidity and temperature requirements indicate that significant losses in alumina extraction would occur if spent shale were stored in ambient Colorado air and allowed to fluctuate naturally in temperature and humidity.

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